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(54) Title: PREPARATION OF RELATIVELY PURE P, P-BISPHENOL S

(57) Abstract

A process of preparing 4,4'-Bisphenol S wherein sulfuric acid is reacted with an excess of phenol while removing water; the product purity is improved with respect to the 2,4'-BPS isomer by adding toluene to the initial product mixture to crystallize and remove the desired 4,4'-BPS. The remaining material is recycled to isomerize the 2,4'-BPS to 4,4'-BPS.

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PREPARATION OF RELATIVELY PURE P,P-BISPHENOL S

Technical Field

This invention relates to the manufacture of p,p-dihydroxydiphenyl sulfone, known also as 4,4'-Bisphenol S (hereafter sometimes "4,4'-BPS"), and particularly to a method of efficiently and/or continuously separating 4,4'-BPS from a product mixture containing significant quantities of 2,4'-BPS, which is typically produced along with the 4,4'-BPS. The basic principle of reacting sulfuric acid with an excess of phenol is known.

Background of the Invention

It is known to react sulfuric acid with an excess of phenol to obtain Bisphenol S. In Ogata et al U.S. Patent 4,820,831 a process is described (col. 4) wherein the phenol/sulfuric acid (dehydration) reaction is conducted in the presence of a solvent which is distilled off along with the excess phenol to promote the production of 4,4'-BPS. In U. S. Patent 4,820,831, Ogata et al also adds an aromatic sulfuric acid to promote isomerization of 2,4'-BPS to 4,4'-BPS. However, there are disadvantages to this procedure, namely that the color of the reaction product deteriorates as the solvent and phenol are removed from the mixture and the colored materials formed as well as any catalysts added must be removed in subsequent purification steps.

In U.S. Patent 4,382,147, Kitamura et al cool the original dehydration reaction product (or, apparently, any mixture of BPS isomers) to separate out the 4,4'-BPS. No particular solvent is used; the 4,4'-BPS is separated as an adduct with phenol.

Summary of the Invention

I have found that the reaction of sulfuric acid and phenol to make BPS can be conducted quite efficiently by (a) forcing the dehydration reaction to completion (or near completion) by gradually distilling a mixture of water and phenol from the reaction mixture, (b) selectively precipitating 4,4'-BPS from the reaction mixture by adding a solvent such as toluene, (c) removing the 4,4'-BPS from the mixture by a separation step, i.e. filtration or centrifugation, and (d) the unrecovered material from the separation step is recycled to the dehydration reaction step. The purity of the product 4,4'-BPS is maintained at a high level by following this process, particularly in the detail described below; the color is excellent.

Solvents which may be used other than toluene are benzene, chlorobenzene, xylene, o-dichlorobenzene, anisole, cumene, and the like.

Detailed Description of the Invention

My invention comprises

(a) reacting sulfuric acid and phenol in a ratio of about 1:2 to about 1:10, preferably about

1:2.5 to about 1:5, at temperatures beginning at about 40 to about 100°C, preferably about 60 to about 70°C, and increasing during the reaction to about 190 to about 205°C, preferably about 195 to about 200°C under an inert atmosphere such as nitrogen or argon, preferably at atmospheric pressure although a vacuum may be used.

(b) during the reaction, removing the water formed by distilling off the water as a mixture with phenol until the reaction is complete, or nearly complete.

(c) adding about 0.1 to about 5.0 equivalent volumes, preferably about 0.5 to about 1.5 volumes (based on the volume of phenol used for the reaction as one equivalent volume), of a solvent for Bisphenol S, preferably benzene, toluene, chlorobenzene, xylene, o-dichlorobenzene, anisole, or cumene, most preferably toluene, over a period of about 10 to about 200 minutes, preferably about 30 to about 60 minutes. During the addition the mixture should be cooled or allowed to cool to the boiling point of the solvent, then the mixture allowed to cool further to about room temperature to about 120°C, preferably about 55 to about 75°C to form crystals of 4,4'-BPS.

(d) separating the crystals of 4,4'-BPS from the reaction mixture preferably by filtration or centrifugation.

(e) isolating the BPS isomers from the filtrate from step (d) by removal of the solvent and phenol and crystallizing the BPS isomers, and

(f) recycling the isolated BPS isomers from step (e) by adding the mixture to reaction

step (a) to bring about isomerization of the 2,4'-BPS contained in the filtrate to 4,4'-BPS during the reaction cycle.

(g) further purifying the crude 4,4'-BPS isolated from separation step (d) above by recrystallizing the compound from water or mixtures of water and solvents such as methanol, ethanol and acetone, preferably methanol. The water or water/solvent mixture should contain about 0.0005 to about 0.05 molar equivalents, preferably about 0.002 to 0.01 molar equivalents (based on the amount of BPS being recrystallized) of a reducing agent such as a thiosulfate, sulfite, bisulfite or borohydride salt, preferably sodium bisulfite, to reduce the amount of color in the final product.

A preferred process ("best mode") is as follows:

(1) Molten phenol (purified, 4.75-5.0 molar equiv.) is placed in the reactor and the system is flushed with an inert atmosphere (nitrogen).

(2) Concentrated sulfuric acid (1.0 molar equiv.) is added to the phenol and the mixture is heated to reflux (155°C) over a period of 30 minutes.

(3) A mixture of water and phenol is slowly distilled off until the reaction temperature reaches 195°C and the distillation head temperature reaches 170°C. This usually takes 2-2.5 hours.

(4) The reaction mixture is then refluxed for an additional 1-1.5 hours, collecting distillate only when the still head temperature falls below 170°C.

(5) Toluene (a volume equivalent to the volume of phenol used in the reaction) is slowly added to the reaction mixture. This cools the reaction mixture to the boiling point of toluene (110°C) and reduces the solubility of BPS in the solution. When the reaction mixture temperature reaches about 130°C and the solvent is approximately 25-30% toluene, the 4,4'-isomer of BPS begins to precipitate from the solution as a fine pink powder. The remainder of the toluene is added while the precipitation continues.

(6) After all the toluene has been added, the mixture is cooled to 65°C and then filtered.

(7) The solid is rinsed with toluene to remove some orange colored material and then dried to yield a light pink powder.

(8) The toluene and most of the phenol are distilled under vacuum from the filtrate from step (6).

(9) Toluene is added to the distillation residue from step (8) to precipitate the 2,4'-BPS isomer and the remainder of the 4,4'-isomer.

(10) The precipitate from the distillation pot residue in step (9) is filtered from the slurry and is then recycled by adding it to a subsequent reaction batch of BPS between steps (2) and (3), above.

(11) An additional one hour reflux period is added to the beginning of step (3) above, before any distillate is collected, for batches of BPS which contain recycled materials to help insure complete equilibration of the BPS isomers during the reaction cycle.

(12) The BPS from step (7) is dissolved in an equivalent weight of boiling methanol and treated with 0.005 molar equivalents of sodium sulfite as a 1.0 molar solution in water. The methanolic solution is then diluted with water (9 times the weight of the methanol used) keeping the mixture at its boiling point. After all of the water has been added the mixture is allowed to cool to room temperature. The solid is removed from the mixture by filtration and rinsed with water and dried to remove the excess solvent.

My process has been used successfully as is illustrated in the following examples of experiments performed:

Example 1

Sulfuric acid (22.62 g, 94.6%) was added to molten phenol (100.41 g) at 70°C with rapid stirring into a reaction flask equipped with a simple distillation apparatus. The mixture was heated to 130°C for one hour and then heated further to reflux temperature (155°C) and a mixture of water and phenol was gradually distilled from the reaction flask until the solution temperature reached 195°C and the distillation head temperature had reached 170°C. The distillate collection was stopped and the mixture was refluxed until the vapor temperature fell to below 160°C. The distillate was collected again until the distillation head temperature again rose to 170°C. The cycle of distillate collection and refluxing was continued until 2.5 hours had elapsed since the first distillate was collected.

Toluene (100 ml) was added over a period of 40 minutes while maintaining rapid stirring. After the addition was complete, the mixture was allowed to cool to 60°C. The product was removed from the suspension by vacuum filtration and rinsed with two portions of toluene (50 ml) and then dried to remove the residual toluene to yield 33.41 g of 4,4'-BPS with a purity of 97.5%.

The crude product was dissolved in boiling methanol (25 ml) and hot water (225 ml) which contained sodium thiosulfate (0.10 g) was added while keeping the mixture boiling. The solution was cooled to 25°C and allowed to crystallize over a period of 3 hours at that temperature. The product was collected by vacuum filtration and the water removed from the crystals to yield 31.72 g of 4,4'-BPS with a purity >99.5% and an APHA color of <20 for a 30% solution in methanol.

Example 2

Sulfuric acid (35.45 g, 93.5%) was added to molten phenol (150.38 g) at 70°C in a reaction flask equipped with a distillation head and the apparatus was evacuated to 350 mm Hg. The mixture was heated to reflux and the distillate was collected any time the distillation head temperature was below 140°C and the distillate collection was stopped any time the vapor temperature rose to 150°C. The reaction mixture was heated in this manner for five hours.

Toluene (150 ml) was added to the reaction mixture over a period of one hour and the mixture was allowed to cool to 65°C before the product was

filtered from the mixture to produce 44.10 g of light pink material which was purified by the means described in Example 1 to give a final product with the >99.5% purity and APHA color of <20 for a 30% methanolic solution.

Example 3

Sulfuric acid (35.20 g, 96.0%) was added to molten phenol (153.30 g) at 70°C in a reaction flask equipped with a Dean-Starke trap and the mixture was heated to 130°C. Cumene (90 ml) was added to the reaction mixture and the solution was heated to reflux, collecting the water of the reaction in the trap and continuously returning the cumene to the reaction vessel. The reaction mixture was refluxed for 7.5 hours at which point the cumene in the Dean-Starke trap was separated from the water and added to the reaction mixture along with an additional 60 ml cumene over a period of 15 minutes. The mixture was gradually cooled to 70°C allowing the product to slowly crystalize. The solid was collected by vacuum filtration, rinsed with two 50 ml portions of cumene and dried to remove the remainder of the solvent to yield 4,4'-BPS (60.1 g, 98.1%). After purification by the method described in Example 1, a product was obtained with a purity >99.5% and an APHA color of <20 for a 30% solution in methanol.

Example 4

Phenol (151.40 g) and sulfuric acid (35.94 g, 96.0%) were reacted in the manner described in Example 1. After the addition of

toluene (150 ml) and cooling of the reaction mixture to 70°C, 4,4'-BPS (52.1 g, 97.7%) was separated from the excess phenol and toluene by vacuum filtration.

The filtrate was distilled under vacuum to remove the toluene and most of the phenol (78 g). The toluene was added to the distillation pot residue, causing the precipitation of a mixture of 2,4'-BPS and 4,4'-BPS (28.1 g).

Phenol (182.2 g) and sulfuric acid (35.2 g) were mixed and heated to 130°C for one hour. The mixture of BPS isomers from above was added to the mixture which was then heated to reflux (155°C) for one hour. The reaction was then carried out as in Example 1 with the mixture of water and phenol distilled off whenever the vapor temperature fell below 160°C. Toluene (180 ml) was added to the mixture and the product was collected after the mixture had cooled to 65°C. The crude 4,4'-BPS (74.2g) was recrystallized as described in Example 1 to produce a material with purity >99.5% and APHA color of 30 for a 30% methanolic solution.

CLAIMS

1. A process for making purified 4,4'-dihydroxydiphenyl sulfone comprising

(a) reacting sulfuric acid and phenol in a ratio of about 1:2 to about 1:10 at temperatures starting at about 40 to about 100°C and increasing during the reaction to temperatures of about 190 to about 205°C,

(b) during the reaction, removing the water formed by codistilling a mixture of water and phenol from the reaction mixture,

(c) adding about 0.1 to about 5.0 equivalent volumes of a solvent for 4,4'-Bisphenol S (based on the volume of phenol used in the reaction as 1.0 equivalent volume) and cooling the mixture to about room temperature to about 120°C to cause formation of crystals of 4,4'-Bisphenol S,

(d) separating the crystals of 4,4'-BPS from the reaction mixture,

(e) further purifying the crystal product by dissolving and recrystallizing the crystal product in mixtures of water and a polar solvent with the addition of about 0.0005 to about 0.05 molar equivalents of a reducing agent, and

(f) recycling at least some of the filtrate from step (d) to the dehydration step (a) after removal of the solvent to bring about the isomerization of the 2,4'-BPS.

2. Process of claim 1 wherein the solvent of step (c) is toluene.

3. Process of claim 1 wherein step (d) is performed by filtration.

4. Process of claim 1 wherein step (d) is performed by centrifugation.

5. Process of claim 1 wherein the solvent of step (e) is methanol.

INTERNATIONAL SEARCH REPORT

International Application No. PCT/US91/04437

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC(5): C07C 315/00
U.S. CL: 568/28

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
U.S.	568/28

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
A	US,A 3,250,812 (GILBERT) 10 May 1966 (10.5.66) See entire document	1-5

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search: 08 January 1992

Date of Mailing of this International Search Report: 16 JAN 1992

International Searching Authority: ISA/US

Signature of Authorized Officer: Robert C. Whittenbaugh

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